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Chemical Reduction and Dimerization of 1-Chloro-2,3,4,5-tetraphenylborole

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Abstract: As neutral isoelectronic analogues of the elusive cyclopentadienyl cation, boroles have been of interest for their prospective applications as strong Lewis acids, chromophores, and electron acceptors. Recently our group discovered a π-nucleophilic boryl anion based on the borole system. In an effort to extend borole chemistry, we now report the molecular structure of 1-chloro-2,3,4,5-tetraphenylborole (**1**) and its corresponding borole dianion resulting from the two-electron reduction of **1** with KC_8. The thermally induced dimerization of **1** yields an unprecedented boracyclohexadiene/borolene spiro-bicyclic compound and the resulting dimer was fully characterized including a single-crystal X-ray analysis.

Keywords: antiaromaticity · boroles · boron · reduction · spiro compounds

Introduction

Functionalized boron-containing π-conjugated systems have attracted considerable attention due to their promising applications in optoelectronics that can be ascribed to the presence of the low-lying empty p orbital at boron.[1] Studies on boracycles have illustrated that the incorporation of boron into a cyclic π-conjugated system has a more pronounced effect on the electronic state of the molecule than for its acyclic analogue.[2] In addition to aromatic boracycles, that is, borirenes[3] and borepines,[4] recent focus has shifted to their counterparts to induce stronger perturbation of the π-system.[5] As the smallest neutral antiaromatic boracycle, borole is extremely electron deficient and requires steric protection of the C_4B core for the isolation of monomeric, non-annulated derivatives.[6] Even though the synthesis of pentaarylboroles was reported in the 1980s, the structural characterization of these compounds was only accomplished very recently.[7] However, the study of boroles was to some extent limited to pentaarylboroles until the recent isolation of 1-chloro- and 1-bromoboroles, which make direct functionalization at the boron atom practical.[7c,8] The presence of the electron-deficient boron center renders borole derivatives strong Lewis acids with potential applications in catalysis, anion sensing, and optoelectronics.[5a,b,e] The increasing research focus on boroles is reflected by the considerable number of reports published in the past two years alone.[7–9] To date, the substituents successfully installed at the boron atom range from aryl groups, halogens, and amino groups, to ferrocenyl and platinum complex fragments.

Two-electron reduction of a borole results in a 6π aromatic Hückel system, isoelectronic to the well-studied cyclopentadienyl anion. Accordingly, the coordination chemistry of the borole dianion as a ligand for transition metals has been a motivation for researchers in the field.[6b,10] However, in spite of the aromatic nature of this boracycle, very few borole dianions have been isolated and structurally characterized; their boron substituents are limited to aryl and amino groups.[7b,11] We recently disclosed the reaction of a carbene-stabilized borole monoanion with methyl iodide, and suggested that this anion may serve as a useful π-boryl anion and boron nucleophile.[12] To broaden our understanding of borole anions, we now report the solid-state structure of 1-chloro-2,3,4,5-tetraphenylborole (**1**), its reduction to the chloroborole dianion, and an unusual dimerization reaction of the chloroborole.

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Results and Discussion

By steric protection of the C_4B core with phenyl groups, the electron-deficient chloroborole **1** can be readily isolated by the boron–tin exchange reaction of BCl_3 with 1,1-dimethyl-2,3,4,5-tetraphenylstannole, as previously described.[8] Single crystals of **1** suitable for X-ray diffraction analysis were obtained as dark green needles from a concentrated CH_2Cl_2 solution at −60 °C.

The results of the X-ray diffraction analysis (Figure 1) confirm the presence of a tricoordinate, planar boron atom in the solid state as indicated by the sum of the angles around B1 of 360.0°. As in pentaarylboroles, a propeller-like arrangement of the phenyl groups with respect to the central C_4B ring is observed.[7] However, no close contacts between B1 and phenyl groups were identified, suggesting the presence of an isolated borole system. The pronounced C−C bond length alternation is consistent with the optimized singlet ground state geometry of antiaromatic pentaarylboroles.[7a,b] The B1−Cl1 distance of 1.7433(14) Å is in the expected range for an sp^2 B−Cl bond, such as in $(C_6F_5)_2BCl$ (1.746(5) Å),[13] $(C_6H_3F_2)_2BCl$ (1.755(2) Å),[14] and $Cp^*{}_2BCl$ (1.790(3) Å).[15]

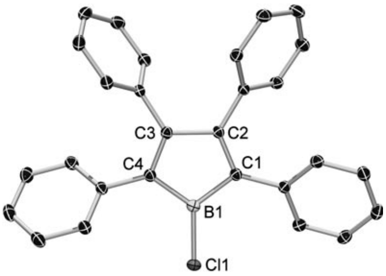
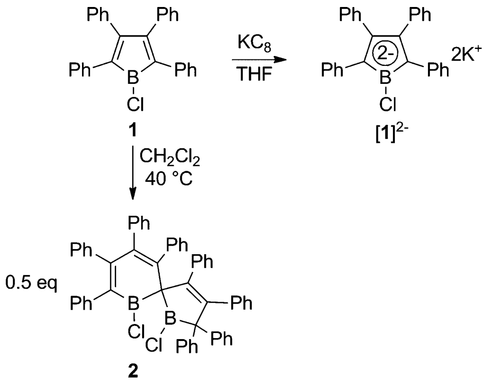


Figure 1. Molecular structure of **1** in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°]: B1–Cl1 1.7433(14), B1–C1 1.5636(18), B1–C4 1.5663(18), C1–C2 1.3619(16), C2–C3 1.5196(17), C3–C4 1.3547(16); C1-B1-C4 107.72(10), B1-C1-C2 104.35(10), C1-C2-C3 111.60(10), C2-C3-C4 111.96(10), C3-C4-B1 104.36(10), C1-B1-Cl1 126.34(9), C4-B1-Cl1 125.94(10).

Chemical reduction of **1** with excess KC_8 in THF affords the corresponding borole dianion $K_2(THF)_2$[**1**], in moderate yield (Scheme 1). $K_2(THF)_2$[**1**] is stable in the solid state under inert atmosphere but extremely sensitive towards air and moisture. As expected, the ^{11}B NMR resonance of $K_2(THF)_2$[**1**] detected at $\delta = 26.6$ ppm is comparable to that observed for $K_2[C_4Ph_4BPh]$.[16] The condensed phase molecular structure of $K_2(THF)_2$[**1**] was also determined by X-ray crystallography. Bright red single crystals of $K_2(THF)_2$[**1**] were obtained from diffusion of hexane into a solution of $K_2(THF)_2$[**1**] in THF at ambient temperature. $K_2(THF)_2$[**1**] crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. Neighboring $K_2(THF)_2$[**1**] units are bridged by a potassium–chlorine interaction to form an extended structure in the solid state (see Figure S1 in the Supporting Information). Within each molecular unit, the borole ring is essentially planar with two potassium atoms located above and below the C_4B plane in a η^5 manner (Figure 2). The propeller arrangement of the phenyl groups with an average tilting angle of 42.16° is typical. The boron atom features a trigonal-planar geometry with the sum of the angles around the boron atom of 360.0°. The B−C and C−C bond lengths within the borole ring are comparable to those measured for $K_2[C_4Ph_4BPh]$, indicative of the 6π-electron aromaticity. The B1−Cl1 bond length of 1.839(4) Å is noticeably elongated compared to that observed in **1** as a result of the electronic repulsion between the π electrons of the borole ring and the lone pairs on the chlorine atom.



Scheme 1. Reduction and dimerization of **1**.

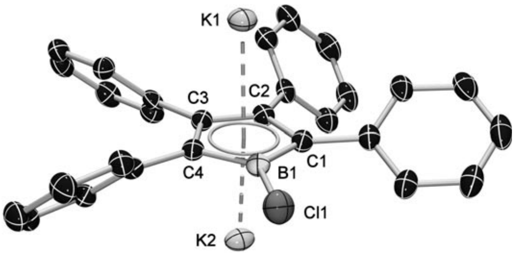


Figure 2. Molecular structure of the K_2[**1**] fragment in $K_2(THF)_2$[**1**] in the solid state with hydrogen atoms and solvent molecules omitted for clarity. Thermal ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°]: B1–Cl1 1.839(4), B1–C1 1.517(6), B1–C4 1.505(6), C1–C2 1.456(5), C2–C3 1.418(5), C3–C4 1.451(5), B1–K1 3.178(4), B1–K2 3.102(4); C1-B1-C4 107.7(3), B1-C1-C2 105.2(3), C1-C2-C3 110.6(3), C2-C3-C4 110.6(3), C3-C4-B1 105.8(3), C1-B1-Cl1 127.4(3), C4-B1-Cl1 124.9(3).

In addition to chemical reduction, a thermal stability study of **1** was performed. Heating a solution of **1** in dichloromethane at 40 °C leads to the formation of a new compound (**2**) after two days (Scheme 1). The ^1H NMR spectrum of **2** contains a complicated splitting pattern between $\delta = 5.80$ to 7.27 ppm. Additionally the ^{11}B NMR resonances of **2**, detected as two broad signals at $\delta = 59.0$ and 74.4 ppm, suggest that compound **1** dimerizes into an asymmetric molecule with two chemically nonequivalent tricoordinate boron centers. Solid-state structural determination of

2 was achieved by single-crystal X-ray analysis. Compound **2** crystallizes from a THF/hexane (1:1) solution at ambient temperature as yellow block crystals. As indicated in Figure 3, compound **2** is a chiral spiro compound that features one five-membered and one six-membered *B*-chloroboracycle. Since the C2–C3, C5–C6, and C7–C8 bond lengths are typical for a C=C bond, the six-membered ring can be described as a boracyclohexadiene,[17] while the five-membered ring is a borolene.[11b] Both boron atoms adopt a trigonal-planar geometry as indicated by the sum of angles around the boron atom of 359.8° and 360.0°, respectively. Notably, the B2–C8 bond is significantly shorter than the other B–C bonds. The B2–C8 bond length of 1.525(2) Å is also shorter than that observed in the 9-dimesitylboryl acridinyl radical (1.559(5) Å), which features a formal one-electron B=C double bond, implying the presence of significant π-bonding character of the B2–C8 bond.[18] Accordingly, the B2–Cl2 bond is slightly longer than the B1–Cl1 bond as a consequence of increased electron density at B2 from the π-electron delocalization of the butadiene backbone.

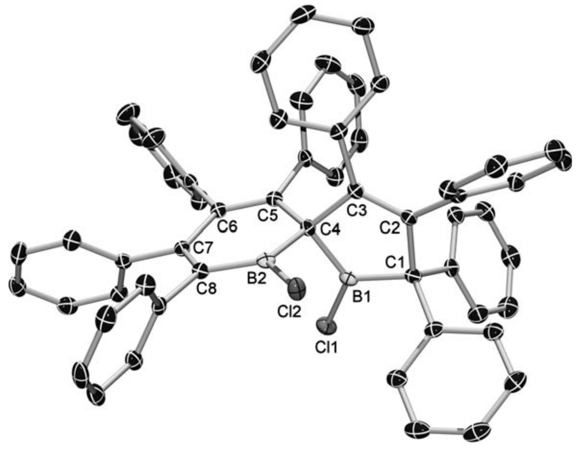
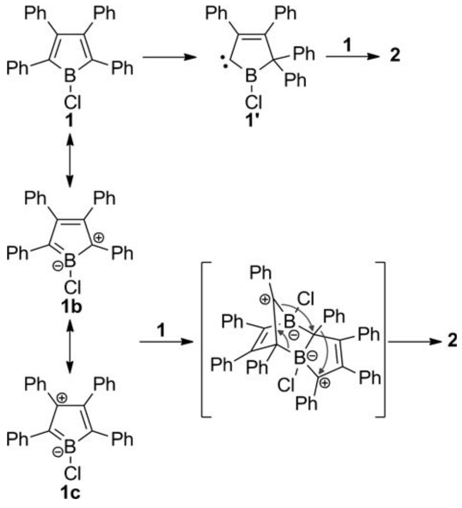


Figure 3. Molecular structure of **2** in the solid state with hydrogen atoms omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: B1–Cl1 1.7527(18), B2–Cl2 1.7741(18), B1–C1 1.594(2), B1–C4 1.591(2), C1–C2 1.542(2), C2–C3 1.346(2), C3–C4 1.540(2), B2–C4 1.586(2), B2–C8 1.525(2), C4–C5 1.511(2), C5–C6 1.354(2), C6–C7 1.477(2), C7–C8 1.373(2); C1-B1-C4 111.46(13), C1-B1-Cl1 124.69(12), C4-B1-Cl1 123.69(12), C4-B2-C8 120.32(14), C4-B2-Cl2 119.48(12), C8-B2-Cl2 120.15(12).

The thermally induced rearrangement/dimerization of **1** is a unique process when compared to other pentaarylborole derivatives, which generally possess good thermal stability even in hot toluene solution.[7b,c] The formation of the spiro compound is also distinct from the [2.2.1]bicycloborole dimers commonly formed by sterically less demanding boroles via a Diels–Alder reaction.[19] Two possible reaction pathways are depicted in Scheme 2. The first one involves a [1,5]-sigmatropic migration of the phenyl group to generate a transient α-borylated carbene species, which subsequently inserts into the B–C bond of the other chloroborole. However, this reaction pathway was ruled out by theoretical calculations on the system. Geometry optimization of **1** and its hypothetical carbene isomer (**1′**) was carried out by DFT methods (B3LYP, 6-31g**). Single-point energy calculations of these two molecules reveal an energy difference of 68 kcal mol^{-1} between **1** and **1′**, which is too high to be overcome under mild heating conditions. Therefore, the carbene insertion reaction pathway is unlikely to occur during the dimerization process of **1**.



Scheme 2. Proposed dimerization mechanism of **1**.

Another proposed reaction pathway is the initial formation of the [2.2.1]bicyclo dimer, in which the addition reaction occurs over the B1–C1 bond instead of the C1–C2 bond. Owing to the strong electron deficiency of the boron atom in boroles there is considerable contribution of the charge-separated zwitterionic formulas **1b** and **1c**, both featuring a B=C double bond and a carbenium center. It is assumed that the cycloaddition took place at the less hindered part of the molecule, that is, the borataalkene moiety, rather than the sterically encumbered C=C double bond. This bicyclic derivative quickly undergoes subsequent phenyl migration and B–C bond rearrangement to form the spiro-bicyclic compound.

Conclusion

In summary, chemical reduction of 1-chloro-2,3,4,5-tetraphenylborole was carried out, and the resulting 1-chloroborole dianion was isolated and structurally characterized. The boracyclohexadiene/borolene spirobicyclic compound **2** was synthesized by thermally induced dimerization of **1**. The detailed dimerization mechanism of **1** is currently under investigation with computational methods in our laboratory.

Experimental Section

General considerations: All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. C_4Ph_4BCl

was prepared according to published procedures.[8] Hexane, THF, and CH_2Cl_2 were dried by distillation over Na/K alloy (hexane, THF) or phosphorus pentoxide (CH_2Cl_2) under argon and stored over molecular sieves. CD_2Cl_2 was degassed with three freeze–pump–thaw cycles and stored over molecular sieves. [D_8]THF was degassed and dried by passing through activated alumina. Elemental analyses were obtained on a Elementar Vario MICRO cube instrument. NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer (500 MHz for ^1H, 160 MHz for ^{11}B, 126 MHz for $^{13}C\{^1H\}$) and a Bruker Avance 400 NMR spectrometer (400 MHz for ^1H, 128 MHz for ^{11}B, 100.5 MHz for $^{13}C\{^1H\}$). Chemical shifts are given in ppm, and are referenced against external Me_4Si (^1H, ^{13}C), and $BF_3{\cdot}Et_2O$ (^{11}B).

Synthesis of $K_2(THF)_2$[1]: THF (1 mL) was added to a mixture of C_4Ph_4BCl (50.0 mg, 124 μmol) and KC_8 (50.0 mg, 370 μmol) at room temperature to give a dark red solution. The mixture was stirred for 10 min and then filtered. Hexane (2 mL) was diffused into the solution over a period of 5 h to give $K_2(THF)_2$[**1**] as a bright red solid, which was washed with cold diethyl ether (0.5 mL) and dried (19.1 mg, 30.6 μmol, 25 %). Single crystals that were suitable for X-ray crystallography were obtained by the same method. ^1H NMR (400 MHz, [D_8]THF): $\delta=6.26$–6.30 (m, 2H), 6.59–6.64 (m, 2H), 6.66–6.71 (m, 4H), 6.76–6.81 (m, 8H), 6.97–7.00 ppm (m, 4H); ^{11}B NMR (128 MHz, [D_8]THF): $\delta=26.6$ ppm (br); $^{13}C\{^1H\}$ NMR (100.5 MHz, [D_8]THF): $\delta=116.4$, 120.6, 121.8, 126.7, 127.0, 129.3, 132.3, 146.0, 149.2 ppm; elemental analysis calcd (%) for $C_{36}H_{36}BClK_2O_2$: C 69.17; H 5.80; found: C 68.15; H 5.61.

Synthesis of 2: C_4Ph_4BCl (47.0 mg, 117 μmol) was dissolved in CH_2Cl_2 (1.5 mL) and heated to 40 °C for 42 h to give a brown solution. The solvent was removed under reduced pressure, hexane (1 mL) was added to the brown residue and stirred for 3 h. The resulting precipitate was filtered, washed with hexane (3 × 1 mL), and dried under vacuum to give $Cl_2B_2C_8Ph_8$ (**2**) (25.0 mg, 31.0 μmol, 52 %) as a yellow solid. Analytically pure crystals suitable for X-ray crystallography were obtained by recrystallization from THF/hexane (1:1). ^1H NMR (500 MHz, CD_2Cl_2): $\delta=$ 5.80–5.82 (m, 1H), 6.04–6.05 (m, 1H), 6.40–6.43 (m, 1H), 6.49–6.51 (m, 1H), 6.62–6.73 (m, 6H), 6.84–6.87 (m, 3H), 6.91–7.06 (m, 15H), 7.09–7.14 (m, 5H), 7.18–7.27 ppm (m, 7H); ^{11}B NMR (160 MHz, CD_2Cl_2): $\delta=$ 59.0 (br), 74.4 ppm (br); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): $\delta=69.9$, 83.7, 125.3, 125.7, 126.1, 126.3, 126.4, 126.5, 126.7, 127.0, 127.2, 127.5, 127.6, 127.7, 128.0, 128.3, 129.6, 129.9, 130.0, 130.4, 130.9, 131.2, 131.6, 132.4, 138.4, 139.6, 140.3, 140.7, 141.1, 141.2, 142.0, 143.3, 145.6, 145.9, 153.4, 165.1 ppm; elemental analysis calcd (%) for $C_{56}H_{40}B_2Cl_2$: C 83.51; H 5.01; found: C 83.20; H 5.20.

Crystal structure determination: The crystal data of **1**, $K_2(THF)_2$[**1**], and **2** were collected on a Bruker X8 APEX diffractometer with a CCD area detector and multilayer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved by using direct methods, refined with the Shelx software package,[20] and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

Crystal data for $1(CH_2Cl_2)_2$: $C_{30}H_{24}BCl_5$, $M_r=572.55$, green needle, 0.32 × 0.13 × 0.10 mm^3, monoclinic space group $P2_1/c$, $a=13.268(5)$, $b=25.573(8)$, $c=8.225(3)$ Å, $\beta=103.277(16)°$, $V=2716.4(16)$ Å^3, $Z=4$, $\rho_{calcd}=1.400$ g cm^{-3}, $\mu=0.553$ mm^{-1}, $F(000)=1176$, $T=100(2)$ K, $R_1=0.0344$, $wR^2=0.0889$, 6517 independent reflections [$2\theta \leq 56.8°$] and 325 parameters.

Crystal data for $K_2(THF)_2$[1]: $C_{72}H_{72}B_2Cl_2K_4O_4$, $M_r=1250.22$, orange plate, 0.20 × 0.09 × 0.02 mm^3, triclinic space group $P\bar{1}$, $a=10.8311(14)$, $b=10.8933(14)$, $c=14.5463(18)$ Å, $\alpha=68.684(2)$, $\beta=77.066(3)$, $\gamma=84.902(3)°$, $V=1558.2(3)$ Å^3, $Z=1$, $\rho_{calcd}=1.332$ g cm^{-3}, $\mu=0.422$ mm^{-1}, $F(000)=656$, $T=103(2)$ K, $R_1=0.0982$, $wR^2=0.2213$, 6134 independent reflections [$2\theta \leq 52.84°$] and 386 parameters.

Crystal data for 2: $C_{56}H_{40}B_2Cl_2$, $M_r=805.40$, yellow plate, 0.20 × 0.13 × 0.04 mm^3, orthorhombic space group $Pbca$, $a=17.9229(16)$, $b=19.9110(18)$, $c=23.771(2)$ Å, $V=8483.1(14)$ Å^3, $Z=8$, $\rho_{calcd}=1.261$ g cm^{-3}, $\mu=0.192$ mm^{-1}, $F(000)=3360$, $T=100(2)$ K, $R_1=0.0546$, $wR^2=0.0903$, 8706 independent reflections [$2\theta \leq 52.88°$] and 541 parameters.

CCDC-779266 (**1**), CCDC-778763 ($K_2(THF)_2$[**1**]), and CCDC-778764 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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